JOC Article

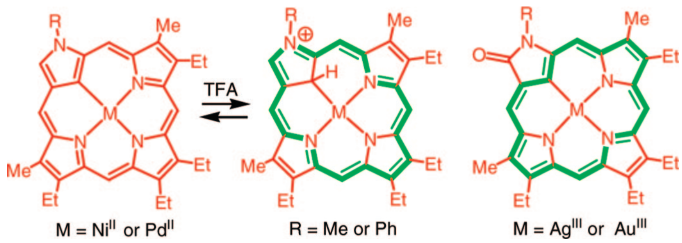
# Synthesis and Reactivity of *N*-Methyl and *N*-Phenyl *meso*-Unsubstituted N-Confused Porphyrins[†]

Timothy D. Lash* and Amber L. Von Ruden

*Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160*

*tdlash@ilstu.edu*

*Received September 14, 2008*




Condensations of 1-methyl and 1-phenyl-2,4-pyrroledicarbaldehydes with a tripyrrane in TFA−dichloromethane, followed by oxidation with aqueous $FeCl_3$, gave novel cross-conjugated *meso*-unsubstituted N-confused porphyrins (NCPs; **12**). These porphyrin analogues showed significant diatropic ring currents that were enhanced upon protonation. Reactions with nickel(II) acetate in refluxing DMF, or palladium(II) acetate in acetonitrile, gave good yields of the corresponding nickel(II) or palladium(II) organometallic derivatives **18** and **19**. These complexes were stable and the proton NMR spectra showed slightly increased downfield shifts to the external protons. Addition of TFA resulted in C-protonation at the internal carbon to give aromatic cations that showed the inner CH resonance between −2.5 and −4.0 ppm. The nickel(II) cations **20a** and **20b** slowly underwent demetalation but the related palladium cations **20c** and **20d** were quite robust and showed no loss of palladium after 1 week at room temperature. Reaction of NCPs **12** with silver(I) acetate gave silver(III) derivatives **21a** and **21b** where an oxidation had occurred at C-3 to afford a lactam unit. The silver complexes showed strong diatropic ring currents and porphyrin-like UV−vis spectra with a Soret band near 430 nm. *N*-Methyl NCP **21a** also reacted with gold(III) acetate to give the gold(III) NCP **21c**, albeit in low yield, and this species showed similar spectroscopic properties to silver(III) NCP **21a**. Syntheses of *N*-phenyl NCP **12b** were accompanied by the formation of the 3-oxo derivative **15b**, and the related *N*-methyl product **16a** could also be obtained when the reaction mixtures were oxidized with silver(I) acetate under acidic conditions. The proton NMR spectra for these aromatic NCPs in $CDCl_3$ show the internal CH shifted upfield to near −6.5 ppm, while the external *meso*-protons are strongly deshielded giving 4 singlets between 9 and 10 ppm. This study demonstrates that *meso*-unsubstituted NCPs have unusual reactivity and unique spectroscopic properties, and these results complement and extend the work on the much better known *meso*-tetraaryl NCPs.

## Introduction

N-confused porphyrins (NCPs; **1**) were first reported as byproducts in Rothemund-type syntheses by two independent groups in 1994.[1,2] These tetrapyrrolic macrocycles differ from true porphyrins by having an inverted pyrrole moiety and a CNNN arrangement of core atoms.[3] NCPs immediately aroused a great deal of interest due to their aromatic character, the presence of relatively long wavelength UV−vis absorptions, and their ability to generate organometallic derivatives under mild conditions.[4] NCPs have two major tautomeric forms, **1** and **2**, that differ in energy by approximately 5 kcal/mol.[5] The fully aromatic tautomer **1** is favored in organic solvents such as chloroform and the proton NMR spectrum for NCPs in $CDCl_3$

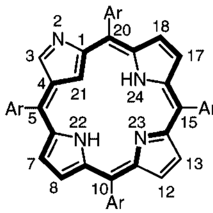
[†] Part 47 in the series "Conjugated Macrocycles Related to the Porphyrins". For part 46, see Lash, T. D.; Colby, D. A.; Idate, A. S.; Davis, R. N. *J. Am. Chem. Soc.* **2007**, *129*, 13800−13801.

(1) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767–768.

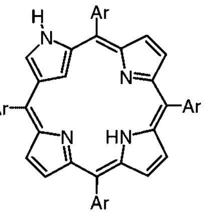
(2) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779–781.

(3) Sessler, J. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1348–1350.

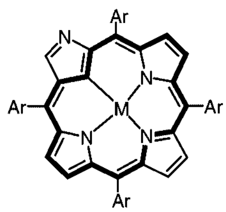
10.1021/jo802040q CCC: $40.75 
Published on Web 11/08/2008



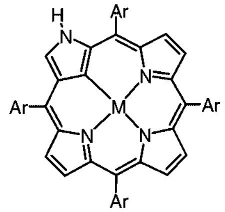
**1** N-confused porphyrins



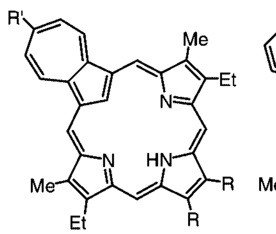
**2**



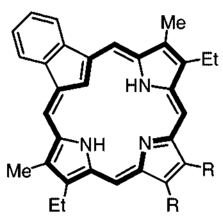
**4** a. M = Ag(III)
b. M = Au(III)



**3** a. M = Ni(II)
b. M = Pd(II)



**5** Azuliporphyrins



**6** Benzocarbaporphyrins

shows the presence of a strong diatropic ring current where the internal CH resonates at −5 ppm, while the external pyrrolic protons give rise to a series of peaks between 8.5 and 9.0 ppm. However, in polar aprotic solvents such as DMF and DMSO, the cross-conjugated tautomer **2** predominates and surprisingly this form has been characterized by X-ray crystallography.[5] Although the diatropicity of **2** is much reduced, the internal CH is still shifted upfield to 0.76 ppm in proton NMR spectra run in $d_6$-DMF.[5] The less aromatic tautomer of the NCPs can be trapped by methylation on the external nitrogen.[6] In addition, NCPs form metallo-derivatives **3** that are derived from tautomer **2** with divalent metal cations such as nickel(II) and palladium(II).[2,7] On the other hand, tautomer **1** can act as a trianionic ligand and form stable organometallic derivatives **4** with metals in higher oxidation states such as silver(III).[8] In parallel with these studies, the synthesis[9−12] and metalation[13−16] of carbaporphyrinoids such as **5** and **6** have been reported. Azuliporphyrins **5** act as dianionic ligands giving stable organometallic derivatives with Ni(II), Pd(II), and Pt(II),[13] and in this respect have comparable reactivity to NCP tautomer **2**. In contrast, benzocarbaporphyrins **6**[14] and related carbaporphyrinoids[15−17] act as trianionic ligands, readily forming silver(III) and gold(III) complexes, and therefore mirror the properties of aromatic NCP tautomer **1**.

The development of a high yielding procedure for synthesizing *meso*-tetrasubstituted NCPs[18] opened up the field and has allowed detailed investigations into the reactivity of these porphyrin isomers.[3,19] However, far less work has been conducted on the synthesis and reactivity of *meso*-unsubstituted NCPs.[20−22] The first synthesis of *meso*-unsubstituted NCPs made use of a MacDonald "2 + 2" procedure, but this method was not suitable for larger scale reactions.[20] Porphyrin analogues like **5** and **6** were synthesized by a "3 + 1" methodology by reacting tripyrranes **7** with aromatic dialdehydes.[23−25] However, initial attempts to prepare NCPs **8** by reacting 2,4-pyrroledicarbaldehydes **9** with tripyrranes under a variety of conditions afforded mediocre yields of porphyrinoid products (Scheme 1).[21] In these reactions, the macrocyclic product is generated as a dihydro derivative and an oxidation step is required to generate the final product. In most of the early studies, DDQ was used for the dehydrogenation step, but this gave very poor results for NCPs **8**. Eventually, washing the reaction solutions with dilute aqueous solutions of ferric chloride was found to be a

(4) (a) Latos-Grazynski, L. Core-Modified Heteroanalogues of Porphyrins and Metalloporphyrins. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, pp 361−416. (b) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795–1804. (c) Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1–19. (d) Chmielewski, P. J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2005**, *249*, 2510–2533.

(5) Furuta, H.; Ishizuka, T.; Osuka, A.; Dejima, H.; Nakagawa, H.; Ishikawa, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6207–6208.

(6) Chmielewski, P. J.; Latos-Grazynski, L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 503–509.

(7) (a) Szterenberg, L.; Latos-Grazynski, L. *Inorg. Chem.* **1997**, *36*, 6287–6291. (b) Furuta, H.; Kubo, N.; Maeda, H.; Ishizuka, T.; Osuka, A.; Nanami, H.; Ogawa, T. *Inorg. Chem.* **2000**, *39*, 5424–5425.

(8) (a) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676–2682. (b) Furuta, H.; Morimoto, T.; Osuka, A. *Org. Lett.* **2003**, *5*, 1427–1430.

(9) Oxybenziporphyrins: (a) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533–2535. (b) Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076–9088. (c) Richter, D. T.; Lash, T. D. *Tetrahedron* **2001**, *57*, 3659–3673.

(10) Benzocarbaporphyrins: (a) Lash, T. D.; Hayes, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 840–842. (b) Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860–4874. (c) Liu, D.; Lash, T. D. *J. Org. Chem.* **2003**, *68*, 1755–1761. (d) Lash, T. D.; Muckey, M. A.; Hayes, M. J.; Liu, D.; Spence, J. D.; Ferrence, G. M. *J. Org. Chem.* **2003**, *68*, 8558–8570.

(11) Azuliporphyrins: (a) Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed.* **1997**, *36*, 839–840. (b) Lash, T. D.; Colby, D. A.; Graham, S. R.; Chaney, S. T. *J. Org. Chem.* **2004**, *69*, 8851–8864. (c) Graham, S. R.; Colby, D. A.; Lash, T. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1371–1374. (d) Colby, D. A.; Lash, T. D. *Chem.−Eur. J.* **2002**, *8*, 5397–5402. (e) Lash, T. D.; Colby, D. A.; Ferrence, G. M. *Eur. J. Org. Chem.* **2003**, 4533–4548. (f) Colby, D. A.; Ferrence, G. M.; Lash, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 1346–1349.

(12) Tropiporphyrins: (a) Lash, T. D.; Chaney, S. T. *Tetrahedron Lett.* **1996**, *37*, 8825–8828. (b) Bergman, K. M.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 7888–7897.

(13) (a) Graham, S. R.; Ferrence, G. M.; Lash, T. D. *Chem. Commun.* **2002**, 894–895. (b) Lash, T. D.; Colby, D. A.; Graham, S. R.; Ferrence, G. M.; Szczepura, L. F. *Inorg. Chem.* **2003**, *42*, 7326–7338.

(14) (a) Muckey, M. A.; Szczepura, L. F.; Ferrence, G. M.; Lash, T. D. *Inorg. Chem.* **2002**, *41*, 4840–4842. (b) Lash, T. D.; Colby, D. A.; Szczepura, L. F. *Inorg. Chem.* **2004**, *43*, 5258–5267.

(15) Lash, T. D.; Rasmussen, J. M.; Bergman, K. M.; Colby, D. A. *Org. Lett.* **2004**, *6*, 549–552.

(16) (a) Liu, D.; Lash, T. D. *Chem. Commun.* **2002**, 2426–2427. (b) Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462–463. (c) Liu, D.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 6079–6093. (d) Miyake, K.; Lash, T. D. *Chem. Commun.* **2004**, 178–179. (e) Lash, T. D.; Pokharel, K.; Serling, J. M.; Yant, V. R.; Ferrence, G. M. *Org. Lett.* **2007**, *9*, 2863–2866.

(17) (a) Stepien, M.; Latos-Grazynski, L.; Lash, T. D.; Szterenberg, L. *Inorg. Chem.* **2001**, *40*, 6892–6900. (b) Stepien, M.; Latos-Grazynski, L. *Chem.−Eur. J.* **2001**, *7*, 5113–5117. (c) Stepien, M.; Latos-Grazynski, L. *Acc. Chem. Res.* **2005**, *38*, 88–98. (d) Szymanski, J. T.; Lash, T. D. *Tetrahedron Lett.* **2003**, *44*, 8613–8616. (e) Lash, T. D.; Szymanski, J. T.; Ferrence, G. M. *J. Org. Chem.* **2007**, *72*, 6481–6492.

(18) Geier, G. R., III.; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **1999**, *1*, 1455–1458.

(19) Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10–20.

(20) Liu, B. Y.; Brückner, C.; Dolphin, D. *Chem. Commun.* **1996**, 2141–2142.

(21) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973–7982.

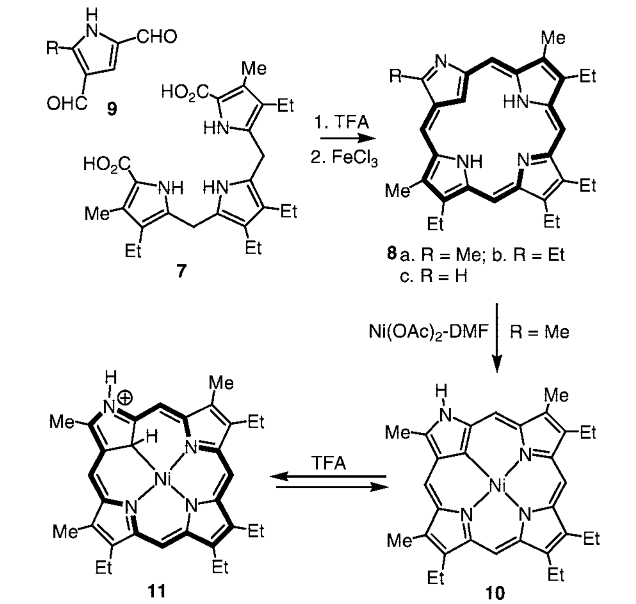
(22) Morimoto, T.; Taniguchi, S.; Osuka, A.; Furuta, H. *Eur. J. Org. Chem.* **2005**, 3887–3890.

(23) Lash, T. D. *Synlett* **2000**, 279–295.

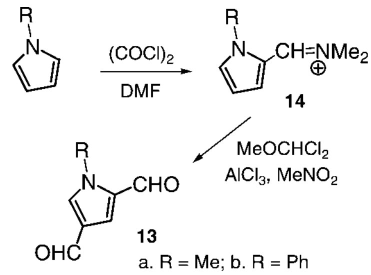
(24) Lash, T. D. Synthesis of Novel Porphyrinoid Chromophores, In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, pp 125−199.

(25) Lash, T. D. *Eur. J. Org. Chem.* **2007**, 5461–5481.

**SCHEME 1**



**SCHEME 2**

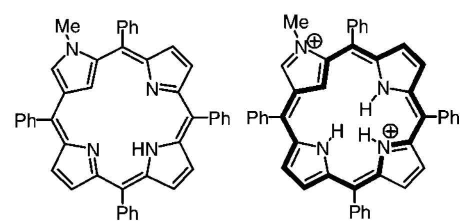


superior oxidation protocol for these syntheses and under optimized conditions up to 61% yield of NCPs **8** could be isolated, although 3-unsubstituted NCP **8c** was only obtained in 16% yield.[21] More recently, a synthesis of fully unsubstituted NCP has also been completed.[22] It is noteworthy that the *meso*-unsubstituted NCPs show significantly larger diatropic ring currents and the internal CH for NCPs **8** in $CDCl_3$ was observed near −6.3 ppm.[21] The increased diatropicity in **8** can be ascribed to a flattening out of the macrocycle due to the relief of steric congestion caused by *meso*-aryl substitution. NCP **8a** was shown to react with nickel(II) acetate in DMF at 145 °C to give the nickel(II) complex **10**, but this metallo-derivative was somewhat unstable and showed little aromatic character.[21] Addition of TFA to an NMR solution of **10** in $CDCl_3$ gave a surprising result where C-protonation at position C-21 occurred to generate an aromatic species **11**. The proton NMR spectrum showed the internal CH resonance at −4.93 ppm, and the *meso*-protons shifted from 7.83−8.68 ppm in **10** to 9.37−10.01 ppm for **11**.[21] This phenomenon was subsequently demonstrated for Ni(II) and Cu(II) complexes derived from *meso*-tetraaryl NCPs as well.[26]

As the field of N-confused porphyrin chemistry has developed, remarkable reactivity features, such as the formation of N-fused porphyrins,[27] have been discovered and a profusion of unusual coordination complexes have been described.[19] Nevertheless, very little work has so-far been conducted on *meso*-unsubstituted NCPs. These versions of NCPs have the potential to extend the reactivity studies while complementing the results obtained for other carbaporphyrinoid systems such as **5** and **6**. In this paper, we describe rational "3 + 1" syntheses of *N*-methyl and *N*-phenyl NCPs **12** and provide details on the oxidation and metalation of these new porphyrinoids.[28]

## Results and Discussion

The synthesis of *N*-substituted NCPs **12** by the "3 + 1" methodology required the availability of pyrrole dialdehydes **13a** and **13b**. For this work, we adapted procedures developed by Anderson et al. for the synthesis of 2,4-pyrroledicarbaldehydes.[29] *N*-Methylpyrrole had previously been shown to react with the Vilsmeier reagent to give an imine salt **14a** and this further reacts with dichloromethyl methyl ether, aluminum chloride and nitromethane to afford, following hydrolysis, the required dialdehyde **13a** (Scheme 2).[29] *N*-Phenylpyrrole was shown to react similarly to give 1-phenyl-2,4-pyrroledicarbaldehyde in 75% yield. Tripyrrane **7** was treated with TFA, diluted with dichloromethane, and dialdehyde **13a** was added. After stirring the mixture for 16 h at room temperature, the solution was oxidized by shaking it with 0.1% aqueous ferric chloride solution in a separatory funnel for 5 min. The crude product was purified by column chromatography on grade 3 basic alumina and recrystallized from chloroform-hexanes to give *N*-methyl NCP **12a** in 39% yield (Scheme 3). Reaction of *N*-phenylpyrrole dialdehyde **13b** with **7** afforded the corresponding *N*-phenyl NCP **12b** together with an oxidation product **15b**. Following careful chromatography on grade 2 neutral alumina, **13b** and **15b** were isolated in 17 and 12% yields, respectively. The formation of lactam-like confused porphyrinoids is well precedented in the literature.[30,31] A plausible mechanism involves initial addition of water to the protonated NCP to give hemiaminal **16**, followed by oxidation to give the oxo-derivative **15** (Scheme 4). As expected, NCPs **12** showed intermediary diatropic character.



**17** $\mathbf{17}H_2^{2+}$

In the proton NMR spectrum for *N*-methyl tetraphenyl NCP **17** in $CDCl_3$, the internal CH is reported to show up at 0.98 ppm and the NH gives rise to a peak at 3.43 ppm. However, in the proton NMR spectrum for **12a**, the 21-CH gave rise to a singlet near 1.5 ppm and the NH showed up as a broad peak at

(26) Chmielewski, P. J.; Latos-Grazynski, L.; Schmidt, I. *Inorg. Chem.* **2000**, *39*, 5475–5482.

(27) (a) Furuta, H.; Ishizuka, T.; Osuka, A.; Ogawa, T. *J. Am. Chem. Soc.* **2000**, *122*, 5748–5757. (b) Toganoh, M.; Ikeda, S.; Furuta, H. *Inorg. Chem.* **2007**, *46*, 10003–10015.

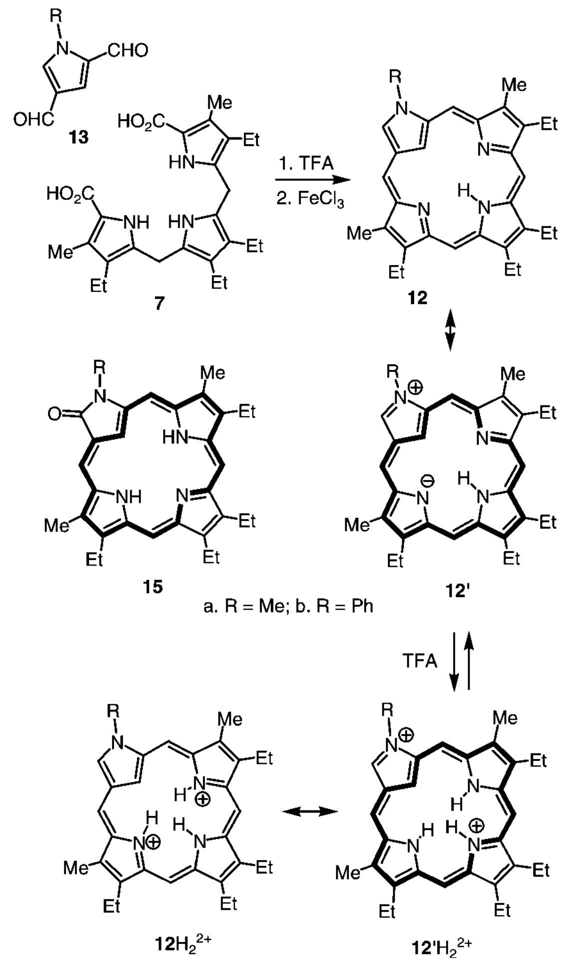
(28) These results were presented, in part, at the following meeting: 233rd National American Chemical Society Meeting, Chicago, IL, March 2007 (Von Ruden, A. L.; Lash, T. D. *Book of Abstracts,* ORGN 192).

(29) Anderson, H. J.; Loader, C. E.; Foster, A. *Can. J. Chem.* **1980**, *58*, 2527–2530.

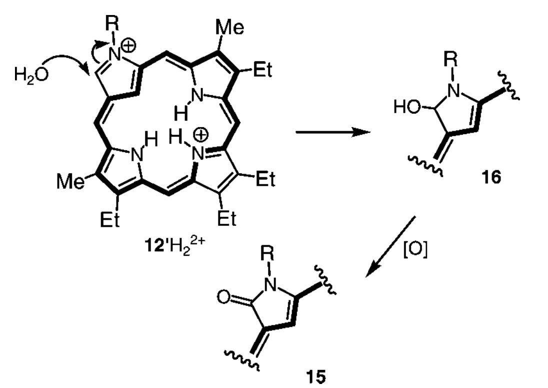
(30) Srinivasan, A.; Ishizuka, T.; Osuka, A.; Furuta, H. *J. Am. Chem. Soc.* **2003**, *125*, 878–879.

(31) Halide anion binding has recently been demonstrated for a protonated *meso*-unsubstituted 3-oxoNCP. See: Furuta, H.; Nanami, H.; Morimoto, T.; Ogawa, T.; Král, V.; Sessler, J. L.; Lynch, V. *Chem. Asian J.* **2008**, *3*, 592–599. We thank a referee for bringing this paper to our attention.

**SCHEME 3**




**SCHEME 4**




2.75 ppm (Figure 1). A $D_2O$ shake showed exchange of the NH but the 21-CH resonance also sharpened and shifted slightly upfield (Figure 1C). A similar effect was previously noted for substituted azuliporphyrins **5**.[32] The reduced diatropic shift for the 21-CH resonance in **12a** compared to **17** was unexpected, as the decrease in macrocyclic planarity due to the presence of *meso*-substituents would be likely to lead to downfield shifts for both the NH and 21-CH resonances. However, computational studies show that the molecular orbitals for *meso*-tetraphenyl NCP differ significantly from unsubstituted NCP,[33] and DFT

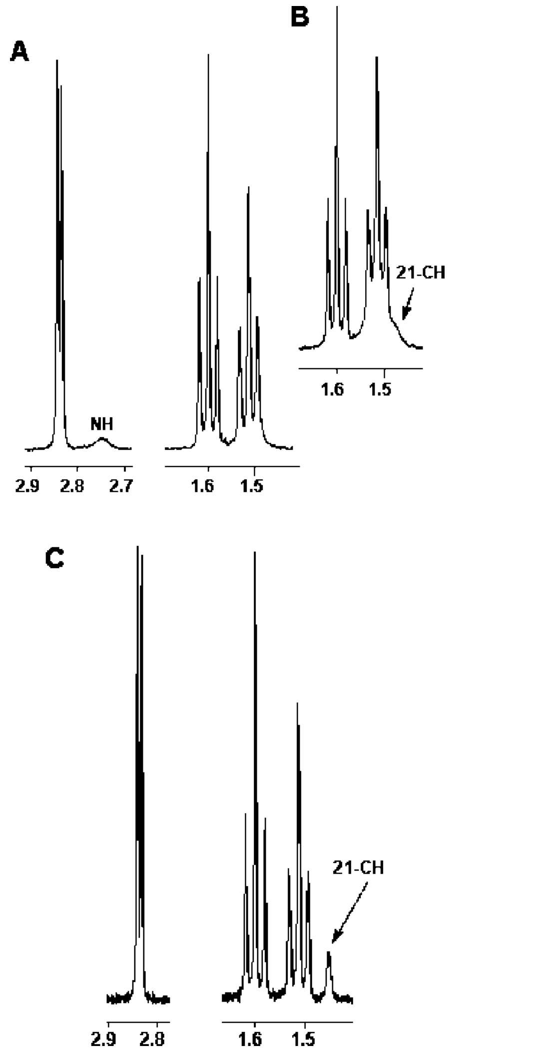



**FIGURE 1.** Partial 400 MHz proton NMR spectra of *N*-methyl NCP **12a** in $CDCl_3$. (A) Upfield region showing the broad NH peak at 2.75 ppm; the 21-CH overlaps with the triplet at 1.5 ppm. (B) Proton NMR spectrum run at a slightly different concentration showing the 21-CH as a broad shoulder. (C) Proton NMR spectrum for the same NMR solution as A after a $D_2O$ shake. The NH peak has been lost and the 21-CH resonance sharpens up and shifts slightly upfield.

calculations indicate that "contributions from the $\pi$ electrons of the phenyl ring are significant" for NCPs **1** and **2**.[34] Therefore, these subtle interactions are likely to be responsible for the small upfield shifts of the inner protons for **17** compared to **12a**. The *N*-phenyl NCP **12b** showed the 21-CH resonance at 2.06 ppm and the NH was identified as a broad peak near 3.9 ppm. The *meso*-protons for **12b** gave rise to 4 singlets between 7.90 and 8.52 ppm, whereas the equivalent resonances for **12a** showed up between 8.00 and 8.50 ppm. Apart from the *meso*-proton that is adjacent to the phenyl group, the resonances for **12a** are further upfield and taken together the diatropic character of **12b** is significantly reduced compared to **12a**. The [18]annulene model for porphyrinoid aromaticity continues to provide valu-

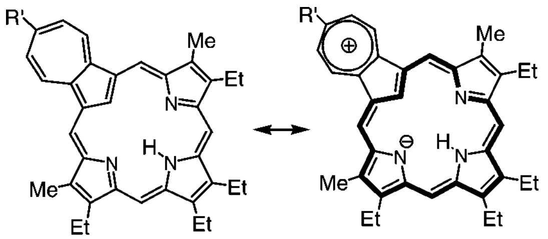
(32) Lash, T. D.; El-Beck, J. A.; Ferrence, G. M. *J. Org. Chem.* **2007**, *72*, 8402–8415.

(33) Belair, J. P.; Ziegler, C. J.; Rajesh, C. S.; Modarelli, D. A. *J. Phys. Chem. A* **2002**, *106*, 6445–6451.

(34) Vyas, S.; Hadad, C. M.; Modarelli, D. A. *J. Phys. Chem. A* **2008**, *112*, 6533–6549.

(35) (a) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257–259. (b) Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406–409.

**SCHEME 5**




5 5'

a. R' = *t*-Bu; b. R' = Ph; c. R = H

able insights into these types of effects.[23,35−38] The *N*-substituted NCPs are cross-conjugated but it is noteworthy that an 18 $\pi$ electron delocalization pathway is present in dipolar resonance contributors like **12′** (Scheme 3). The required electron-donation from the confused pyrrolic nitrogen is clearly aided by the more electron-donating methyl group in **12a** compared to the phenyl unit in **12b**. This trend has also been observed for *tert*-butyl and phenyl substituted azuliporphyrins **5** (Scheme 5).[39] The azulene moiety in **5** is electron-donating and gives the azuliporphyrins a degree of aromatic character due to zwitterionic resonance contributors **5′** which combine tropylium character with a carbaporphyrin-like 18$\pi$ electron delocalization pathway. Although the shifts for **5** are not as large as those observed for NCPs **12**, the internal CH is still shifted upfield to approximately 3 ppm. In the *tert*-butylazuliporphyrin **5a**, the 21-CH gave a resonance at 2.9 ppm but the less electron-donating phenyl moiety in **5b** decreased the contribution of canonical form **5′** and gave this singlet at 3.3 ppm. Observations of this type further emphasize the close relationship of the NCPs, azuliporphyrins and other carbaporphyrinoid systems.

Addition of TFA to NMR solutions of **12a** in $CDCl_3$ gave the corresponding dication **12a**$H_2^{2+}$, and this showed a greatly increased diatropic ring current by proton NMR spectroscopy. The 21-CH resonance shifted upfield to −2.8 ppm and two broad peaks were observed at 0.9 (1H) and 1.1 ppm (2H) for the three NHs (Figure 2). The increased diatropic character is due to the increased favorability of resonance structures like **12′** which are no longer hampered by charge separation but instead aid in charge delocalization. Nevertheless, the presence of an electron-donating methyl group is beneficial. This explains why the shifts for N-phenyl NCP dication **12b**$H_2^{2+}$ are decreased compared to **12a**$H_2^{2+}$, and the 21-CH now gives a signal at −2.05 ppm that is weakly coupled to the C-3 doublet ($J = 1$ Hz) at 8.96 ppm, while the NH resonances are observed at 0.9 (1H) and 1.9 ppm (2H). This effect is also evident in the downfield shifts for the *meso*-protons, which show up as 4 singlets between 9.06 and 9.72 ppm for **12a**$H_2^{2+}$, while three of these values are shifted upfield to between 8.94 and 9.06 ppm for **12b**$H_2^{2+}$. Only the resonance for the *meso*-proton next to the phenyl moiety is an outlier, giving rise to a singlet at 9.70 ppm. Dication **17**$H_2^{2+}$ in excess TFA−$CDCl_3$ is reported to give a resonance for the 21-CH at −1.57 ppm and three peaks for the NHs at 2.05, 2.91 and 3.25 ppm, so in this case the *meso*-tetraphenylNCP shows decreased diatropicity. This can be attributed to the crowding due to the presence of four hydrogen atoms in the macrocyclic cavity exacerbating the steric effects due to the *meso*-substituents.

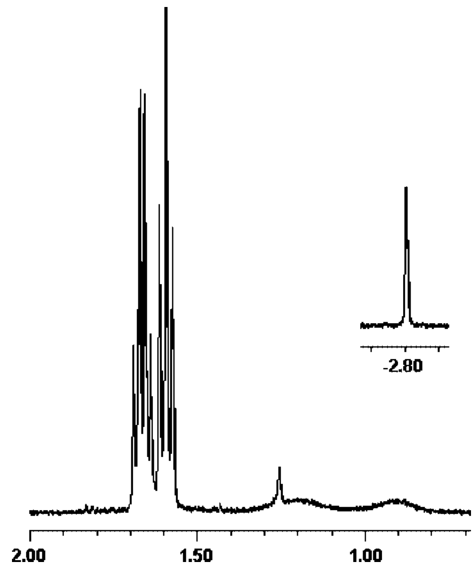



**FIGURE 2.** Upfield region of the 400 MHz proton NMR spectrum for dication **12a**$H_2^{2+}$ in TFA−$CDCl_3$. The broad resonances near 1 ppm correspond to the three internal NHs and the singlet at −2.8 ppm is due to the 21-CH.

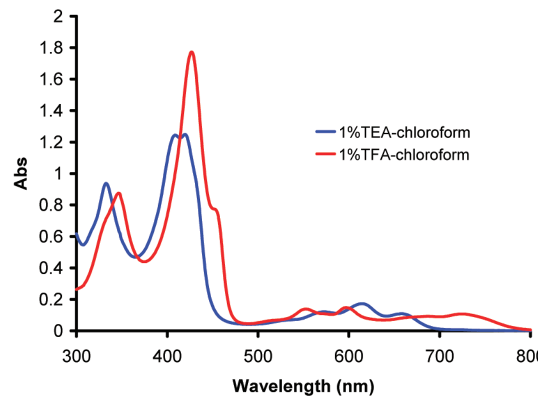



**FIGURE 3.** UV−vis spectra for NCP **12a**. Blue line: free base in 1% $Et_3N$-$CHCl_3$. Red line: Dication **12a**$H_2^{2+}$ in 1% TFA−$CHCl_3$.

The UV−vis spectra for **12a** showed two moderate absorption bands at 409 and 420 nm and weaker broadened absorptions over the visible region (Figure 3). Addition of TFA generated dication **12a**$H_2^{2+}$ and gave a stronger Soret band at 427 nm with a shoulder at 453 nm and a series of Q bands between 500 and 800 nm. PhenylNCP **12b** showed a similar spectrum for the free base, with a weakened Soret-like band at 420 nm, but this again showed a more intense absorption band at 431 nm for the dication **12b**$H_2^{2+}$.

Metalation of the new NCPs **12** was investigated using nickel(II) and palladium(II) acetate (Scheme 6). The best results for incorporating nickel(II) were obtained by refluxing **12a** or **12b** with $Ni(OAc)_2$ in DMF. The earlier work on the synthesis of **10** had to be carried out at 145 °C because extensive decomposition occurred at the slightly higher boiling temperature of DMF. However, better yields of nickel(II) derivatives were obtained under the higher temperature conditions, and following column chromatography on basic alumina and recrystallization, the nickel derivatives **18** were isolated in 76−90% yield. Reactions of **12** with $Pd(OAc)_2$ were carried

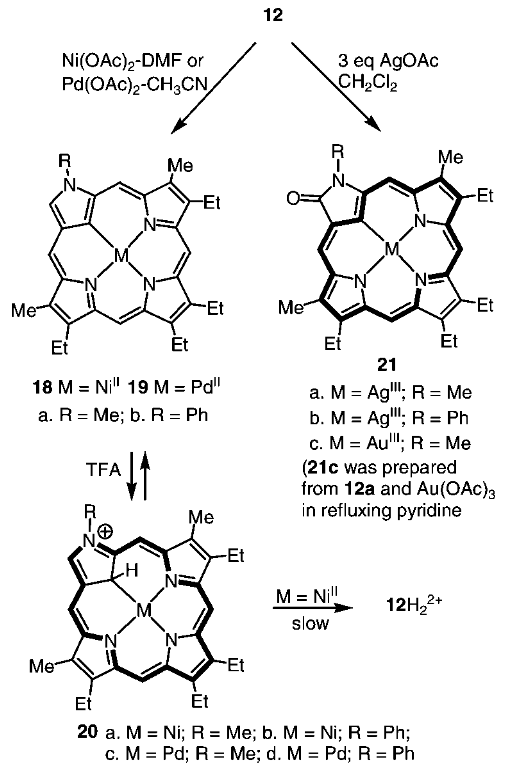
(36) The validity of this type of interpretation for these types of macrocyclic systems is generally supported in the literature[34,36] and while it is considered to be a naïve model, theoretical studies also support these interpretations.[37]

(37) Wannere, C. S.; Corminboeuf, C.; Allen, W. D.; Schaefer, H. F., III.; Schleyer, P. v. R. *Org. Lett.* **2005**, *7*, 1457–1460.

(38) Aihara, J.-i. *J. Phys. Chem. A* **2008**, *112*, 5305–5311.

(39) El-Beck, J. A.; Lash, T. D. *Eur. J. Org. Chem.* **2007**, 3981–3990.

**SCHEME 6**



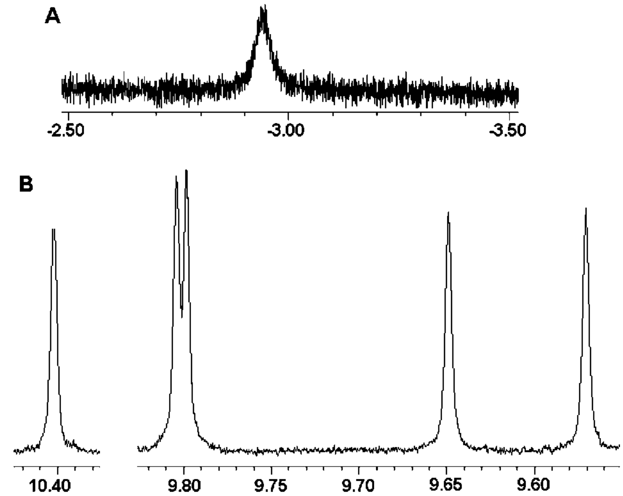




**FIGURE 4.** Partial proton NMR spectrum of palladium complex **19a** in TFA−$CDCl_3$. (A) Spectrum shows an upfield resonance near −3 ppm for the internal CH of the diatropic cation **20c**. (B) External pyrrole and *meso*-protons are strongly deshielded as expected for this aromatic species.

out in refluxing acetonitrile and the palladium(II) complexes **19** were isolated in 58−63% yield. Unlike the moderately unstable nickel(II) complex **10**, the new nickel and palladium derivatives were robust and stable in solution for prolonged periods of time. The proton NMR spectra for **18** and **19** showed the *meso*-protons between 8.32 and 8.84 ppm, values that are significantly downfield from the free base species **12**, but these chemical shifts were similar for the methyl and phenyl series. The chemical shifts are shifted slightly downfield for the palladium complexes **19** compared to the nickel derivatives **18**, and this small effect can be attributed to the increased planarity expected for the organopalladium species.

Addition of a trace amount of TFA to an NMR solution of **18a** in $CDCl_3$ showed a large downfield shift to the *meso*-protons and the external pyrrole CH, giving five 1H singlets at 9.41, 9.45, 9.61, 9.98, and 10.19 ppm, and a broad upfield resonance was observed near −4.0 ppm. These observations are consistent with the formation of an aromatic C-protonated complex **20a**. Further addition of TFA caused the upfield peak to sharpen up but otherwise did not significantly alter the proton NMR spectrum. The nickel(II) complex of the 2-phenylNCP (**18b**) also showed C-protonation on the internal carbon to give **20b** but it was necessary to add several drops of TFA to resolve the upfield resonance. The same phenomenon was observed for palladium(II) complex **19a** which also gave C-protonation to form **20c** and like **18b** this complex required the addition of several drops of TFA to show the upfield resonance (Figure 4). Finally, palladium complex **19b** showed no protonation in the presence of trace amounts of TFA but turned bright green in the presence of 2 drops of TFA and again showed an upfield resonance on addition of larger quantities of acid. The trends show that the nickel(II) complexes undergo protonation more easily than the palladium derivatives, and the *N*-methyl complexes react more readily than the *N*-phenyl species. The increased reactivity of the *N*-methyl series can again be attributed to stabilization of the product due to the presence of a more electron-donating substituent. The protonation of **18** and **19** is reversible, but in the case of nickel(II) derivatives **20a** and **20b** slow demetalation occurs over a period of several hours to give the NCP dications $12H_2^{2+}$. However, the palladium complexes showed little sign of decomposition even after a week at room temperature. The nickel derivatives showed larger upfield shifts for the 21-CH resonance than for the palladium cations, but the downfield signals for the palladium cations were more deshielded. In the methyl series, nickel(II) derivative **20a** gave an upfield resonance at −4.01 ppm, compared to −2.97 ppm for palladium complex **20c**. However, the five downfield singlets for **20c** fell into the range of 9.56−10.42 ppm compared to 9.41−10.19 ppm for **20a**. These data show that the palladium cations are more diatropic than the nickel species, and the differences in the chemical shifts for the 21-CH resonance can be attributed to the higher electronegativity of Pd compared to Ni. The phenyl substituted cations **20b** and **20d** showed a decreased upfield shift for the 21-CH resonance and a decreased downfield shift for the *meso*-proton resonances due to the reduced electron-donating capabilities of the phenyl substituent.

The UV−vis spectra of the nickel(II) derivatives **18** and palladium(II) complexes **19** differed considerably from one another (Figure 5), as had been observed previously for metalated azuliporphyrins,[13,31,39] but the *N*-methyl and *N*-phenyl complexes were very similar in each case. For instance, nickel derivative **18b** gave two stronger absorptions at 342 and 406 nm, together with a shoulder at 454 nm and a prominent peak at 557 nm. Palladium complex **20b** gave a more complex spectrum with three stronger peaks in the Soret region and a series of smaller bands between 500 and 750 nm. Addition of TFA to **18a** gave a spectrum with two bands at 327 and 406 nm, and a broad band between 500 and 600 nm, that corresponds to the aromatic cation **20b** (Figure 5A). In the case of **19b**, addition of TFA gave bright green solutions of **20d** that showed a strong broad band at 437 nm and weaker broad absorptions between 500 and 650 nm (Figure 5B). Again the methyl and phenyl substituted versions for each metal gave similar UV−vis absorption spectra.

The formation of silver derivatives was also investigated (Scheme 6). Tetraphenyl NCP[8] and many carbaporphyrinoid

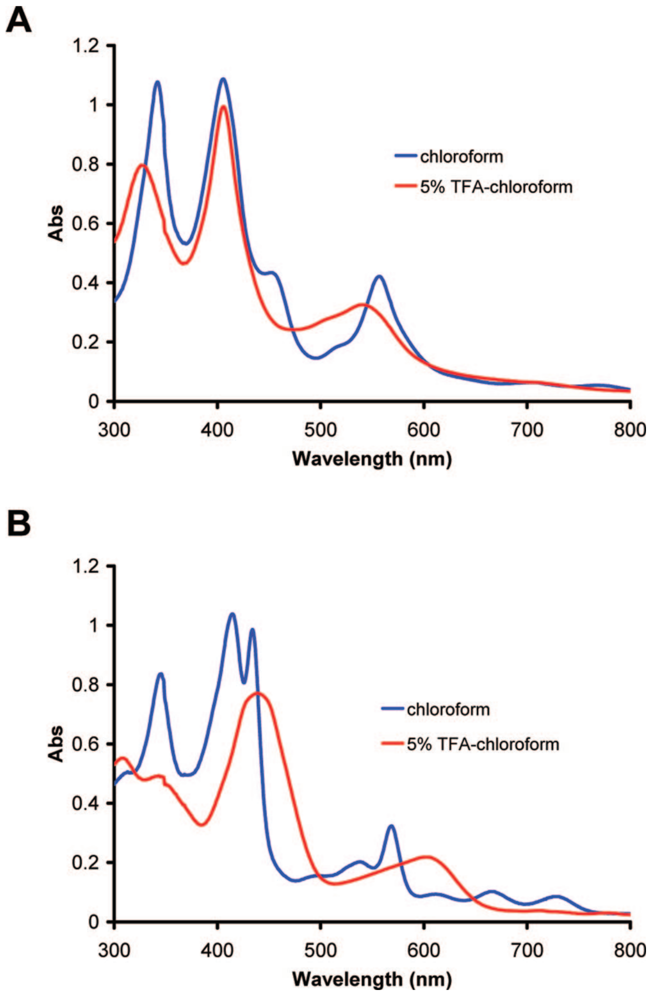



**FIGURE 5.** (A) UV−vis spectra of nickel complex **18b**. Blue line: metal complex in $CHCl_3$; red line: cation **20b** in 5% TFA−chloroform. (B) UV−vis spectra of palladium complex **19b**. Blue line: metal complex in $CHCl_3$; red line: cation **20d** in 5% TFA−chloroform.

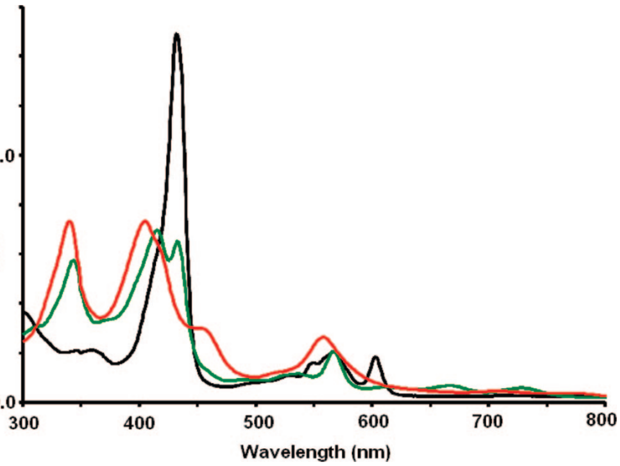



**FIGURE 6.** UV−vis spectrum of silver complex **21a** in chloroform (black line). These data are contrasted to the UV−vis spectra of nickel complex **18a** (red line) and palladium complex **19a** (green line) which do not show the strong porphyrin-like Soret band produced by **21a**.

systems[14−16] easily form silver(III) derivatives, although porphyrins generally afford silver(II) complexes.[40] *N*-Methyl NCP **12a** was treated with 3 equiv of silver(I) acetate at room temperature in dichloromethane and following workup and purification gave a metallo-porphyrinoid product in 65% yield. The complex was only sparingly soluble in organic solvents and it was not possible to obtain a carbon-13 NMR spectrum. However, the proton NMR spectrum in $CDCl_3$ showed only four 1H singlets at 9.10, 9.65, 9.74, and 9.86 ppm, no evidence for the presence of an internal NH or CH were observable, and the 3H singlets corresponding to the two methyl groups were shifted downfield to 3.48 and 3.50 ppm. These data show that the silver complex has taken on a fully aromatic carbaporphyrinoid structure unlike the nickel and palladium complexes **18** and **19**, respectively. The UV−vis spectrum for the silver complex (Figure 6) showed the presence of a strong Soret band at 429 nm and a series of Q-type bands that confirm that this species has porphyrin-like aromatic characteristics. Nevertheless, the external hydrogen on the confused pyrrole unit has been lost and HR MS demonstrated that an oxygen atom had been incorporated and that the molecular formula was $C_{31}H_{34}N_4OAg$. The IR spectrum showed that a prominent absorption was present at 1677 $cm^{-1}$, confirming the presence of a carbonyl moiety. These data indicate that the product is the silver(III) lactam-type NCP **21a**, and that the silver acetate had acted as an oxidant as well as a source of silver ions. This is consistent with the observation that the oxo-derivative **15b** was formed as a byproduct in the synthesis of NCP **12b** (Scheme 3). *N*-Phenyl NCP **12b** also reacted with silver(I) acetate to give silver(III) complex **21b**. In this case, the product was sufficiently soluble to obtain carbon-13 NMR data in $CDCl_3$, and a resonance for the carbonyl unit was identified at 169.5 ppm. The UV−vis spectrum of **21b** was slightly red-shifted compared to **21a**, and showed a strong Soret band at 432 nm.

As silver(I) acetate is acting as an oxidant during metalation, we speculated that it could be used under acidic conditions to prepare the free base porphyrinoid **15a** (Scheme 3). Tripyrrane **7** was reacted with dialdehyde **13a** in the presence of TFA in dichloromethane and then treated with AgOAc. Following column chromatography and recrystallization, lactam **15a** was isolated in 11% yield. The oxo-species was very aromatic by proton NMR spectroscopy, although like its silver(III) derivative **15a** had poor solubility characteristics. The proton NMR spectrum of **15a** in $CDCl_3$ showed the internal CH strongly shifted upfield to −6.63 ppm, while the NHs gave a broad 2H signal centered on −3.9 ppm. The *meso*-protons produced four 1H singlets in the downfield region at 9.06, 9.64, 9.73, and 9.83 ppm (Figure 7). The presence of a porphyrin-like aromatic ring current was also supported by the downfield shifts for the peripheral substituents and the pyrrolic methyl groups gave two 3H singlets at 3.47 and 3.50 ppm. As expected, the UV−vis spectrum for the free base **15a** was porphyrin-like showing two Soret bands at 421 and 435 nm and Q bands at 517, 556, 607, and 667 nm. The related *N*-phenyl oxo-species **15b** has similar spectroscopic properties giving a porphyrin-like UV−vis spectrum and a highly diatropic proton NMR spectrum. Addition of trace amounts of TFA to solutions of **15a** or **15b** gave the corresponding cations **15**$H^+$. The cations showed similar diatropic ring currents in their proton NMR spectra and the UV−vis spectra were still porphyrin-like. The UV−vis spectrum for **15a**$H^+$ in 1% TFA−$CDCl_3$ showed two Soret bands at 427 and 456 nm and a broad band at longer wavelengths. The proton NMR spectrum of **15a**$H^+$ in trace TFA−$CDCl_3$ shows the 21-CH resonance at −6.46 ppm and three 1H singlets for the NHs

(40) Brückner, C. *J. Chem. Educ.* **2004**, *81*, 1665–1669.

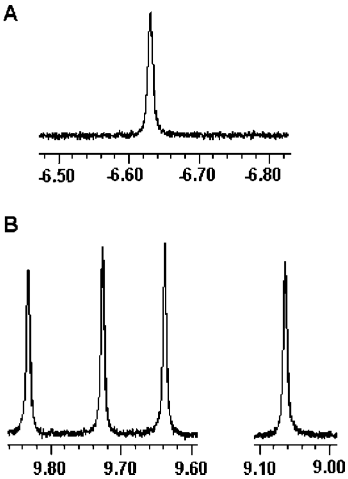
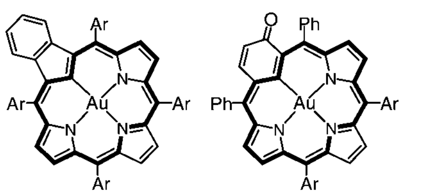



**FIGURE 7.** Partial 400 MHz proton NMR spectrum of the *N*-methyl NCP lactam **15a** in $CDCl_3$ showing the strongly shielded internal CH at −6.6 ppm and the external *meso*-protons downfield between 9 and 10 ppm.

at −3.85, −3.16, and −2.43 ppm. The *meso*-protons are strongly shifted into the downfield region showing four 1H singlets at 9.55, 9.89, 10.08, and 10.20 ppm, and the methyl substituents are also still strongly deshielded giving rise to two 3H singlets at 3.44 and 3.49 ppm.




22 23

a. Ar = Ph; b. Ar = 4-$ClC_6H_4$

In previous studies on the metalation of carbaporphyrinoid systems, we have demonstrated that gold(III) derivatives of tetraaryl benzocarbaporphyrins **22**[14] and oxybenziporphyrins **23**[41] can easily be prepared using gold(III) acetate as a reagent. A *meso*-unsubstituted benzocarbaporphyrin gold(III) complex was also isolated but very poor yields were obtained in this case.[14] Attempts to prepare gold(III) NCPs from **12a** and **12b** gave poor results as well, but the reaction of **12a** with $Au(OAc)_3$ in refluxing pyridine did give an 8% yield of the gold complex **21c**. The chemical shifts in the proton NMR spectrum of **21c** in $CDCl_3$ were very similar to those obtained for silver(III) complex **21a**, and the UV−vis spectrum of **21c** was also comparable, although the Soret band was split into two peaks at 419 and 436 nm. Interestingly, the synthesis of a gold(III) complex of tetraphenyl NCP (**4b**) has only accomplished very recently.[42] The complex, which is reported to have unique luminescence properties, had to be prepared from a brominated intermediate rather than directly from tetraphenyl NCP.[42]

## Conclusions

Two examples of cross-conjugated N-confused porphyrins were prepared by the "3 + 1" methodology using *N*-methyl and *N*-phenyl pyrroledicarbaldehydes. These *meso*-unsubstituted NCPs showed intermediary diatropic properties that were magnified upon protonation in TFA−$CDCl_3$. Reactions with $Ni(OAc)_2$ or $Pd(OAc)_2$ under mild conditions gave the corresponding nickel(II) and palladium(II) organometallic derivatives, and all four of these complexes underwent C-protonation to form an aromatic cation. Reactions with AgOAc gave good yields of the 3-oxo silver(III) complexes **21a** and **21b**, where the silver reagent acts as an oxidant as well as providing the metal cation. However, reactions with $Au(OAc)_3$ gave poor yields of the corresponding gold(III) complex **21c**. Oxidation of the NCP macrocycle could also be accomplished without metalation, and fully aromatic lactam-type NCPs were also isolated and characterized. This study demonstrates that the chemistry of *meso*-unsubstituted NCPs complements and extends the results obtained for better known carbaporphyrinoids systems such as the azuliporphyrins and the *meso*-tetraaryl NCPs.

## Experimental Section

**8,12,13,17-Tetraethyl-2,7,18-trimethyl-2-aza-21-carbaporphyrin (12a).** Tripyrrane dicarboxylic acid **7**43 (100 mg; 0.22 mmol) was stirred with TFA (1 mL) under nitrogen for 2 min. The mixture was diluted with dichloromethane (99 mL) and 1-methyl-2,4-pyrroledicarbaldehyde (32.8 mg; 0.24 mmol) was immediately added in a single portion. The resulting solution was stirred overnight under nitrogen and then washed with water, 0.1% ferric chloride solution, water, and saturated sodium bicarbonate (the aqueous solutions were back-extracted with chloroform at each stage in the extractions). The solvent was removed under reduced pressure and the residue chromatographed on grade 3 basic alumina, eluting with 1% methanol-chloroform. The solvent was removed under reduced pressure and the residue recrystallized from chloroform-hexanes to yield 2-methyl N-confused porphyrin (39.3 mg; 0.085 mmol; 39%) as dark blue crystals, mp >300 °C; UV−vis (1% $Et_3N$−$CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 333 (4.69), 409 (4.82), 420 (4.82), 571 (sh, 3.82), 614 (3.96), 657 nm (3.76); UV−vis (1% TFA−$CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 346 (4.66), 427 (4.97), 453 (sh, 4.61), 553 (3.86), 597 (3.89), 724 nm (3.75); $^1H$ NMR ($CDCl_3$): $\delta$ 1.50 (1H, br s), 1.49−1.54 (6H, 2 overlapping triplets), 1.60 (6H, t, $J$ = 7.2 Hz), 2.75 (1H, br s), 2.83 (3H, s), 2.84 (3H, s), 3.23−3.30 (4H, 2 overlapping quartets), 3.43 (4H, q, $J$ = 7.6 Hz), 4.52 (3H, s), 7.98 (1H, s), 8.00 (1H, s), 8.28 (1H, s), 8.33 (1H, s), 8.47 (1H, s); $^1H$ NMR (TFA−$CDCl_3$, dication): $\delta$ −2.80 (1H, s), 0.93 (1H, br s), 1.25 (2H, br s), 1.59 (6H, t, $J$ = 7.2 Hz), 1.64−1.69 (6H, 2 overlapping triplets), 3.24 (3H, s), 3.25 (3H, s), 3.62−3.72 (8H, m), 4.78 (3H, s), 8.91 (1H, s), 9.06 (1H, s), 9.08 (1H, s), 9.57 (1H, s), 9.72 (1H, s); $^{13}C$ NMR ($CDCl_3$): $\delta$ 10.7, 16.5, 16.6, 17.1, 19.1, 19.19, 19.23, 35.2, 92.9, 93.5, 104.1, 113.2, 122.0, 132.4, 136.6, 139.0, 139.3, 140.0, 140.3, 141.3, 141.7; $^{13}C$ NMR (TFA−$CDCl_3$, dication): $\delta$ 11.22, 11.26, 15.9, 16.7, 19.3, 19.4, 19.5, 37.2, 95.0, 95.4, 104.9, 107.9, 116.8, 123.0, 132.8, 140.8, 141.7, 141.9, 142.1, 142.3, 143.3, 144.7, 145.3, 145.4, 147.1, 147.3, 148.8, 149.6; HR MS (FAB): Calcd for $C_{31}H_{36}N_4$ + H: 465.3018. Found: 465.3018. Anal. calcd for $C_{31}H_{36}N_4 \cdot {}^1/_8CHCl_3$: C, 77.95; H, 7.59; N, 11.68. Found: C, 77.77; H, 7.49; N, 11.49.

**[8,12,13,17-Tetraethyl-2,7,18-trimethyl-2-aza-21-carbaporphyrinato]nickel(II) (18a).** Nickel(II) acetate tetrahydrate (12 mg; 0.048 mmol) was added to a solution of 2-methyl N-confused porphyrin **12a** (22.0 mg; 0.048 mmol) in DMF (24 mL), and the solution was stirred under reflux for 30 min. The solution was cooled, diluted with chloroform, and washed with water. The organic layer was separated, evaporated to dryness, and the residue chromatographed on grade 3 basic alumina, eluting with chloroform, to give a dark red band. The solvent was evaporated and the residue recrystallized from chloroform-methanol to yield the nickel(II) complex (22.2 mg; 0.043 mmol; 89%) as dark purple crystals, mp >300 °C;

(41) El-Beck, J. A.; Lash, T. D. *Org. Lett.* **2006**, *8*, 5263–5266.
(42) Toganoh, M.; Niino, T.; Furuta, H. *Chem. Commun.* **2008**, 4070–4072.
(43) (a) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394–4397. (b) Lash, T. D. *J. Porphyrins Phthalocyanines* **1997**, *1*, 29–44.

UV−vis ($CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 340 (4.95), 405 (4.95), 418 (infl, 4.89), 453 (sh, 4.55), 516 (4.15), 558 (4.51), 710 (3.77), 772 nm (3.70); UV−vis (5% TFA−$CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 324 (4.84), 407 (4.99), 540 nm (4.43); $^1$H NMR ($CDCl_3$): $\delta$ 1.51−1.56 (6H, m), 1.59−1.64 (6H, m), 2.91 (3H, s), 2.92 (3H, s), 3.32−3.45 (8H, m), 4.46 (3H, s), 8.37 (1H, s), 8.41 (1H, s), 8.45 (1H, s), 8.52 (1H, s), 8.59 (1H, s); $^1$H NMR (TFA−$CDCl_3$): $\delta$ −4.01 (1H, br s), 1.63−1.69 (6H, m), 1.72−1.77 (6H, m), 3.20 (3H, s), 3.21 (3H, s), 3.60−3.74 (8H, m), 5.11 (3H, s), 9.41 (1H, s), 9.45 (1H, s), 9.61 (1H, s), 9.98 (1H, s), 10.19 (1H, s); $^{13}$C NMR ($CDCl_3$): $\delta$ 10.9, 11.0, 16.4, 16.8, 17.36, 17.43, 19.2, 19.36, 19.41, 35.0, 95.4, 95.9, 101.9, 111.6, 115.5, 123.9, 134.1, 136.8, 137.8, 140.0, 140.7, 142.9, 144.1, 144.4, 144.8, 148.6, 149.8, 151.3, 153.1; HR MS (EI): Calcd for $C_{31}H_{34}N_4Ni$: 520.2137 Found: 520.2133. Anal. calcd for $C_{31}H_{34}N_4Ni \cdot {}^1/_5CHCl_3$: C, 68.73; H, 6.32; N, 10.27. Found: C, 68.77; H, 6.56; N, 9.99.

**[8,12,13,17-Tetraethyl-2,7,18-trimethyl-2-aza-21-carbaporphyrinato]palladium(II) (19a).** Palladium(II) acetate (26.9 mg; 0.12 mmol) was added to a solution of 2-methyl N-confused porphyrin **12a** (55.7 mg; 0.12 mmol) in chloroform (200 mL), and the solution was stirred under reflux for 30 min. The solution was washed with water, and the organic layer separated and then evaporated to dryness. The residue was chromatographed on grade 3 basic alumina, eluting with chloroform, and the product collected as a reddish/brown band. The solvent was evaporated to dryness and recrystallized with chloroform-methanol to yield the palladium(II) complex (43.0 mg; 0.076 mmol; 63%) as dark purple crystals, mp >300 °C; UV−vis ($CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 344 (4.91), 415 (4.99), 433 (4.96), 537 (4.22), 567 (4.47), 611 (3.94), 666 (3.98), 728 nm (3.91); UV−vis (5% TFA−$CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 310 (4.73), 429 (4.92), 602 nm (4.33); $^1$H NMR ($CDCl_3$): $\delta$ 1.56−1.61 (6H, 2 overlapping triplets), 1.62−1.67 (6H, 2 overlapping triplets), 2.98 (3H, s), 2.99 (3H, s), 3.39−3.52 (8H, m), 4.48 (3H, s), 8.41 (1H, s), 8.46 (1H, s), 8.488 (1H, s), 8.492 (1H, s), 8.65 (1H, s); $^1$H NMR (TFA−$CDCl_3$): $\delta$ −2.97 (1H, br s), 1.73−1.83 (12H, m), 3.31 (6H, s), 3.73−3.83 (8H, m), 5.17 (3H, s), 9.56 (1H, s), 9.64 (1H, s), 9.81 (1H, s), 9.84 (1H, s), 10.42 (1H, s); $^{13}$C NMR ($CDCl_3$): $\delta$ 10.8, 10.9, 16.3, 16.6, 17.3, 19.1, 19.2, 19.4, 19.5, 35.0, 96.1, 96.4, 104.2, 113.4, 120.8, 131.4, 135.6, 136.5, 139.1, 140.1, 142.1, 143.5, 145.1, 146.8, 148.3, 148.6; HR MS (EI): Calcd for $C_{31}H_{34}N_4Pd$: 568.1818 Found: 568.1813. Anal. calcd for $C_{31}H_{34}N_4Pd \cdot {}^1/_5CHCl_3$: C, 63.20; H, 5.81; N, 9.45. Found: C, 63.40; H, 5.97; N, 9.07.

**Silver(III) Complex of 2-Methyl-3-oxo-N-confused Porphyrin (21a).** Three equivalents of silver(I) acetate (21.5 mg; 0.13 mmol) were added to a solution of 2-methyl N-confused porphyrin **12a** (20 mg; 0.043 mmol) in dichloromethane (40 mL), and the solution was stirred at room temperature overnight under nitrogen. The solution was washed with water, and the organic layer was separated and evaporated to dryness. The purple residue was chromatographed on grade 3 basic alumina, eluting with chloroform, and afforded a dark red band. The solvent was evaporated to dryness and the residue recrystallized from chloroform-methanol to yield the silver(III) complex (16.4 mg; 0.028 mmol; 65%) as greenish metallic crystals, mp >300 °C; UV−vis ($CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 359 (4.50), 432 (5.35), 529 (4.21), 547 (4.38), 568 (4.49), 603 nm (4.44); UV−vis (1% TFA−$CHCl_3$): $\lambda_{max}$ ($\log_{10}\epsilon$) 364 (4.56), 429 (5.29), 526 (4.20), 566 (4.42), 599 nm (4.35); IR: $\nu_{C=O}$ 1677 cm$^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 1.77−1.85 (12H, m), 3.48 (3H, s), 3.50 (3H, s), 3.90−4.02 (8H, m), 4.24 (3H, s), 9.10 (1H, s), 9.65 (1H, s), 9.74 (1H, s), 9.86 (1H, s); HR MS (EI): Calcd for $C_{31}H_{34}N_4OAg$: 584.1705. Found: 584.1702. Anal. calcd for $C_{31}H_{34}N_4OAg \cdot {}^1/_5CHCl_3$: C, 61.50; H, 5.49; N, 9.19; Found: C, 61.36; H, 5.52; N, 8.93.

**Acknowledgment.** This material is based upon work supported by the National Science Foundation under Grant No. CHE-0616555 and the Petroleum Research Fund, administered by the American Chemical Society.

**Supporting Information Available:** Experimental procedures for compounds **12b**, **13a**, **13b**, **15a**, **15b**, **18b**, **19b**, **21b**, and **21c**, and MS, UV−vis, $^1$H NMR, and $^{13}$C NMR spectra for selected compounds, are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

JO802040Q